HYDROGENOLYSIS OF ACETALS OF 3-CHLOROTETRAHYDROFURAN SERIES BY ETHEREAL SOLUTION OF CHLOROALANE*

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Acetals of 3-chlorotetrahydrofuran series are cleaved by the action of an ethereal solution of chloroalane either at the endocyclic C—O bond to the corresponding 4-alkoxy-3-chloro-1-butanols, or at the exocyclic C—O bond to 3-chlorotetrahydrofuran and the corresponding alcohol or phenol. Acetals, containing substituents with σ^* smaller than 0·3 are cleaved exclusively at the endocyclic C—O bond whereas compounds with substituents having σ^* greater than, or equal to, 0·6 are cleaved solely at the exocyclic C—O bond. LFER correlations show that, whereas the cleavage of 2-alkoxy-3-chlorotetrahydrofurans is controlled by the decomposition of the acetal–chloroalane complex to the corresponding alkoxycarbenium ions, the cleavage of 3-chloro-2-phenoxytetrahydrofuran is controlled by the formation of an acetal–chloroalane complex.

Many functional groups, resistent to the action of lithium aluminium hydride, have been successfully reduced with lithium aluminium hydride–aluminium chloride mixtures ("mixed hydrides")[1,2]. According to the ratio of components, the active reducing agents are alane and chloroalanes[3]. Most of the data about these reagents are available from studies of the reduction of single C—O bonds in epoxides[4], acetals[5–11], ketals[5,12–16], spiroketals[17], thioacetals[18], thioketals[19] and orthoesters[5]. The results and the assumed course of these hydrogenolyses are directly related to the reactions of similar systems with other reagents of Lewis acid character, which are capable of anion transfer, as *e g.* the reduction of acetals with trialkylsilane–zinc chloride mixture[20], cleavage of ketals with Grignard reagents[21] and hydrogenolysis of acetals and ketals with borane[22]. Concerning the acetals of tetrahydrofuran series, the behaviour of 2-alkoxytetrahydrofurans towards dichloroalane-aluminium chloride[9] and towards chloroalane is already known[10]; also the reactions of 2-alkoxy-5-alkyl- or aryl-substituted tetrahydrofurans[10] and 2-aryloxytetrahydrofurans with chloroalane[11] have been described.

In this paper we investigate the reaction of acetals of 3-chlorotetrahydrofuran series (*I*) with an ethereal solution of chloroalane. The recent opinion on the course

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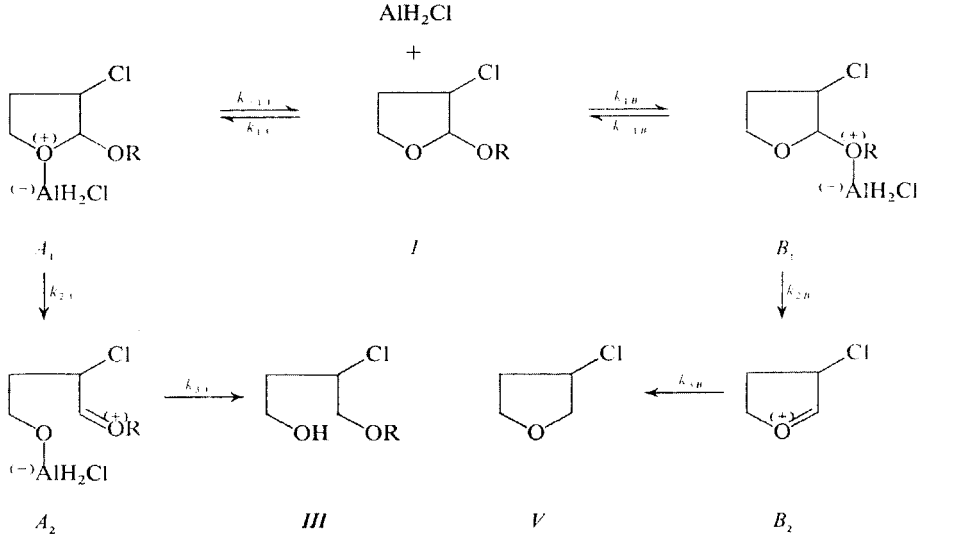
of C—O bond hydrogenolyses, applied by us to the studied reaction of compounds *I* with chloroalane, is expressed by Scheme 1. The first reaction step is assumed to be reversible formation of a complex between basic centers of the substrate and alane or halogenoalane, characterised in the Scheme by the rate constants k_{1A} and k_{-1A} for the pathway *A* (*i.e.* for the complexation of the endocyclic oxygen atom) and k_{1B} and k_{-1B} for the pathway *B* (*i.e.* the complexation of the exocyclic oxygen atom). Further reaction step is then the decomposition of the complexes A_1 and B_1 into the corresponding alkoxycarbenium ions A_2 and B_2, characterised in the Scheme by the rate constants k_{2A} and k_{2B}. In the following fast step (rate constants k_{3A} and k_{3B}), hydride ion is transferred from chloroalane to the alkoxycarbenium ions A_2 and B_2. The irreversibility of this last step (constants k_3) under the reaction conditions is evident; the irreversibility of the decomposition of the complexes A_1 and B_1 to A_2 and B_2 was proved by Leggetter and Brown[14] in the case of *cis*- and *trans*-2,4-disubstituted 1,3-dioxolanes and was assumed also in the hydrogenolyses of isobutylene-ketal of norcamphor[12] and 1,2-O-isopropylidene-3,5,6-O-orthoacetyl-α-D-glucofuranose[5]. As seen from the Scheme, the studied reaction is considerably similar to the acid hydrolysis of acetals, ketals and orthoesters[23], the latter reaction differing of course in that the steps, analogous to that denoted by the constants k_2 and k_3, are reversible.

Generally, the path, as well as the rate, determining step is supposed to be the formation of alkoxycarbenium ions[6,8,9–11,13,16,17,19] A_2 and B_2, characterised by the constants k_2. However, some experimental data can be explained on this basis only using modifying assumptions: *e.g.* cleavage of 2-aryloxytetrahydrofurans ex-



SCHEME 1

clusively at the exocyclic C—O bond[1] (pathway *B*), regiospecific cleavage of 2-aryloxytetrahydropyranes[6,9] (again *via* pathway *B*), cleavage of 2-tetrahydrofuryl and 2-tetrahydropyranyl thioethers[18], 1,3-oxathiolanes and 1,3-thiadioxanes[19] exclusively at the C—O bond, cleavage of 4-phenyl-1,3-dioxolane[16], 2,2-dimethyl-4-phenyl-1,3-dioxolane[16] and 2,2,4,4-tetramethyl-1,3-dioxolane[15,16], *etc.*

The first reaction step, *i.e.* the complex formation, described by the constants k_1, is considered explicitely to be of some importance only in the hydrogenolysis of dimethylketals of medium-ring (C_8-C_{12}) cycloalkanones[7], in order to explain their low reactivity relative to cycloheptanone dimethylketal.

We are of the opinion that such an assumption is considerably simplified, particularly because the complexes A_1 and B_1, and the alkoxycarbenium ions A_2 and B_2 arising from them cannot be regarded as species to which the Hammond postulate is applicable[24]. We think that one can assume situations in which the more stable complex A_1 gives rise to the less stable alkoxycarbenium ion A_2, whereas the more stable alkoxycarbenium ion B_2 arises from the less stable complex B_1, and *vice versa*.

Let us consider for the reaction of *I* with chloroalane the kinetics of formation of the intermediates A_2 and B_2 (which react further very rapidly) according to Scheme 1, using the already introduced symbols. Assuming an equimolar concentration of the starting compounds and practically equilibrium ratio of the complexes A_1 and B_1 during the reaction, we derive the expression (*1*):

$$A_2/B_2 = k_{1A} \cdot k_{2A} \cdot k_{-1B}/k_{1B} \cdot k_{2B} \cdot k_{-1A} \cdot \qquad (1)$$

It follows from the relation (*1*) that the overall rate, as well as the reaction pathway, is determined particularly by the ratios k_{2A}/k_{-1A} and k_{2B}/k_{-1B}, *i.e.* the ratios of the decomposition rates of the complexes A_1 and B_1 back into the starting compounds to the rates of their decomposition into the alkoxycarbenium ions A_2 and B_2.

In the particular and limiting case of the hydrogenolysis of 2-tetrahydrofuryl cyclohexyl thioether, the pathway *A* begins with the complexation of the oxygen atom and the pathway *B* with the complexation of the sulphur atom. The complex A_1 is substantially more stable than the complex B_1 whereas the alkylthiocarbenium ion A_2 is much less stable than the ion B_2. If the difference between the stability of A_1 and B_1 is so great that the concentration of B_1 in the mixture is almost zero, the reaction product will be 4-hydroxybutyl cyclohexyl sulphide. This was really found experimentally[18].

EXPERIMENTAL

The temperature data are uncorrected. The gas–liquid chromatographic measurements were carried out on a Chrom 3 (Laboratorní přístroje, Prague) instrument, equipped with a catharometer; columns 0·6 cm internal diameter, packed with 15% SE 30W on Chromosorb 30/60, carrier gas hydrogen. The analyses were carried out at constant temperatures as well

TABLE I

Reaction of the Acetals *I* with Chloroalane and the Obtained 4-Alkoxy-3-chloro-1-butanols (*III*), 3-Chlorotetrahydrofuran (*V*) and 4-(2-Ethoxy)-1-butanol (*IV*)

Acetal	B.p., °C/Torr n_D^{20}	Ref. time (h)	Product %	B.p., °C/Torr n_D^{20}	Formula (mol.wt.)	Calculated/Found		
						% C	% H	% Cl
Ia	64—67/25	26	*III*	94—96/20[a]	$C_5H_{11}ClO_2$	43·32	8·22	25·57
	1·4462	5	74	1·4505	(136·8)	43·20	8·29	24·93
Ib	73—75/26	27	*III*	93—95/11[a]	$C_6H_{13}ClO_2$	46·25	8·23	23·48
	1·4439	7	66	1·4518	(152·6)	46·58	8·87	23·15
Ic	72—73/27	27	*III*	102—103/20[a]	$C_7H_{15}ClO_2$	50·30	9·07	21·22
	1·4408	5	64	1·4460	(166·6)	50·35	9·16	21·01
Id	68/15	27	*III*	115/15[a]	$C_8H_{17}ClO_2$	53·17	9·48	19·62
	1·4449	15	80	1·4510	(180·7)	53·23	9·31	19·35
Ie	125—127/21	27	*III*	168—171/1[a]	$C_{10}H_{19}ClO_2$	58·54	8·83	16·77
	1·4760	7	75	1·4441	(206·7)	58·69	9·37	16·22
If	137—141/30	28	*III*	167—168/0·8[a]	$C_8H_{16}Cl_2O_2$	44·77	7·49	32·96
	1·4720	12	70	1·4762	(215·1)	44·98	7·74	33·10
Ig	110—111/15	29	*III*	130/2·5[a]	$C_6H_{12}Cl_2O_2$	38·52	5·92	37·97
	1·4756	85	46	1·4772	(187·1)	38·34	5·81	37·53
Ih	115/20	30	*IV*	115—120/25[a]	$C_8H_{18}O_3$	59·18	11·19	—
	1·4522	40	82	1·4373	(162·2)	58·88	11·08	
Ii	126—128/17	[a]	*V*	45—47/11[b]	—	—	—	—
	1·5349	5	58	1·4548				
Ij	61/25	[a]	*V*	46—47/11[b]	—	—	—	—
	1·3957	40	85	1·4552				

[a] This paper, [b] ref.[31].

as using temperature programming. The NMR-spectra were measured on a Tesla BS 487 instrument in deuteriochloroform solutions (unless otherwise stated) with tetramethylsilane as internal standard. The activity of the lithium aluminium hydride (Lachema, Brno) was determined before the reaction by titration of its ethereal solutions with iodine according to Felkin[25]. Anhydrous aluminium chloride (analytical grade, Lachema, Brno) was sublimed *in vacuo* before use. The acetals of the 3-chlorotetrahydrofuran series (*Ia*—*Ih*) were prepared by alcoholysis of 2,3-dichlorotetrahydrofuran (*II*) according to references cited in Table I; their purity was checked by gas–liquid chromatography.

3-Chloro-2-phenoxytetrahydrofuran (*Ii*)

The compound *II* (0·50 mol) was added to a sodium phenoxide solution (prepared from 0·35 mol of phenol and sodium methoxide from 0·35 mol of metallic sodium) in acetone (100 ml) maintaining the temperature of the reaction mixture below 30°C. After standing overnight the mixture was filtered and the product distilled, yielding 21% of the compound *Ii*. For $C_{10}H_{11}ClO_2$ (198·7) calculated: 60·44% C, 5·58% H, 17·84% Cl; found: 60·38% C, 5·71% H, 17·57% Cl.

3-Chloro-2-trifluoroethoxytetrahydrofuran (*Ij*)

Several drops of concentrated hydrochloric acid were added to a solution of the compound *Ib* (10 ml) in an ethanol–trifluoroethanol mixture (1 : 1) and the solution was refluxed. Five hours were sufficient for establishing the equilibrium, at which the mixture contained 24% of the compound *Ij*. The mixture was shaken with an aqueous sodium carbonate solution, extracted with ether, the ethereal extract dried, concentrated and the compound *Ij* was isolated in 19% yield using preparative gas–liquid chromatography. The compound *Ij* was also prepared in 67% yield

TABLE II

Relative Reaction Rates of Acetals of the 3-Chlorotetrahydrofuran Series (*I*) with Chloroalane and the Product Composition at 100% Conversion

Acetal	R	$k_{rel.}$	% *III*	% *V*
cis-Ia	CH_3	0·30	—	—
trans-Ia	CH_3	0·12	—	—
Ia	CH_3	0·42	100	
Ib	C_2H_5	0·55	100	—
Ic	iso-C_3H_7	0·68	100	—
Id	tert-C_4H_9	1·00	100	—
Ie	cyclo-C_6H_{11}	0·57	100	—
If	$(CH_2)_4Cl$	0·37	100	—
Ig	$(CH_2)_2Cl$	0·23	54	6[a]
Ih	$(CH_2)_2OC_2H_5$	0·10	—	[b]
Ii	C_6H_5	0·35	—	100
Ij	CH_2CF_3	0·10	—	100

[a] 20% *IIIb* and 20% *VI*; [b] 100 *IV*.

by alcoholysis of *II* with trifluoroethanol. For $C_6H_8ClF_3O_2$ (204·6) calculated: 35·27% C, 3·94% H; found: 35·16% C, 3·81% H. NMR-spectrum (CCl_4): 3·81 (q, J = 9·0 Hz, 1 H, $H_{CH_2CF_3}$), 3·93 (q, J = 9·0 Hz, 1 H, $H'_{CH_2CF_3}$), 5·11 (s, 1 H, H_α), 4·27 (m, 1 H, H_β), 2·17 (m, 1 H, $H_{\beta'}$), 2·59 (m, 1 H, $H_{\beta''}$), 4·09 (m, 1 H, $H_{\alpha'}$), 4·16 (m, 1 H, $H_{\alpha''}$). where H_α and H_β are the respective protons at alkoxyl and chlorine.

Hydrogenolysis of Acetals of the 3-Chlorotetrahydrofuran Series (*I*) with Ethereal Solution of Chloroalane

An ethereal solution of lithium aluminium hydride (200 ml of 1M solution) was slowly added under nitrogen to 1M ethereal solution of aluminium chloride (200 ml) with cooling to 0—5°C. The mixture was stirred for 15 minutes and a solution of the acetal *I* (0·2 mol) in ether (30 ml) was added slowly without cooling. The mixture was refluxed, cooled, decomposed with 10% aqueous sulphuric acid and neutralized with aqueous sodium carbonate solution. The ethereal layer was separated and the aqueous one was extracted many times with 75 ml portions of ether. The combined ethereal layers were dried over $MgSO_4$, taken down under normal pressure and distilled *in vacuo*. The physical constants and analytical data of the obtained products are given in Table I. The purity of all the prepared 4-alkoxy-3-chloro-1-butanols (*III*) was checked by gas–liquid chromatography. NMR-spectra: *IIIa* (CCl_4): δ 1·86 (m, 2 H, CH_2CCl), 3·36 (s, 3 H, OCH_3), 3·59 (d, J = 6·0 Hz, 2 H, $ClCCH_2O$), 3·65 (s, 1 H, OH), 3·70 (m, 2 H, CH_2O), 4·12 (m, 1 H, CHCl); *IIIb*: δ 1·21 (t, J = 7·0 Hz, 3 H, CH_3), 2·01 (m, 2 H, CH_2CCl), 3·00 (t, 1 H, OH), 3·53 (q, J = 7·0 Hz, 2 H, OCH_2 in the alkyl), 3·64 (d, J = 5·5 Hz, 2 H, $ClCCH_2O$), 3·81 (m, 2 H, CH_2O), 4·19 (m, 1 H, CHCl); *IIIc* (CCl_4): δ 1·16 (d, J = 6·0 Hz, 6 H, 2 CH_3), 1·92 (m, 2 H, CH_2CCl), 2·45 (s, 1 H, OH), 2·62 (m, 5 H, OCH, OCH_2, $ClCCH_2O$), 4·07 (m, 1 H, CHCl); *IIId*: δ 1·17 (s, 9 H, 3 CH_3), 1·91 (m, 2 H, CH_2CCl), 3·20 (s, 1 H, OH), 3·52 (m, 2 H, $ClCCH_2O$), 3·65 (m, 2 H, CH_2O), 4·05 (m, 1 H, CHCl); *IIIe*: δ 1·12—2·25 (m, 12 H, 5 CH_2 of cyclohexane ring, CH_2CCl), 2·56 (s, 1 H, OH), 3·12—3·88 (m, 5 H, CHO, $ClCCH_2O$, CH_2O), 4·17 (m, 1 H, CHCl); *IIIf* (CCl_4); δ 1·50—2·31 (m, 6 H, CH_2CH_2 of the alkoxyl, CH_2CCl), 2·56 (broad s, 1 H, OH), 3·33—3·88 (m, 8 H, CH_2OCH_2, CH_2Cl, CH_2O), 4·10 (m, 1 H, CHCl); *IIIg*: δ 2·01 (m, 2 H, CH_2CCl), 2·97 (s, 1 H, OH), 3·76 (m, 8 H, CH_2O, $CH_2OCH_2CH_2Cl$), 4·25 (m, 1 H, CHCl); *IV* (CCl_4): δ 1·16 (t, J = 6·5 Hz, 3 H, CH_3), 1·57 (m, 4 H, CH_2CH_2), 3·32—3·75 (m, 11 H, CH_2OH, $CH_2OCH_2CH_2OCH_2$). The NMR spectra were simplified by measurement with tris(dipivaloylmethane) europium.

Hydrogenolysis of Acetals of 3-Chlorotetrahydrofuran Series (*I*) with Ethereal Solutions of Alane, Chloroalane, Dichloroalane and Dichloroalane–Aluminium Chloride Mixtures

The acetal *I* (0·01 mol) was treated with a twofold excess of the reducing agent, obtained by mixing ethereal solutions of lithium aluminium hydride and aluminium chloride in the ratios 3 : 1, 1 : 1, 1 : 3 or 1 : 4. The reaction mixture was refluxed till the acetal *I* was not detectable. For the acetals *Ia*—*If* and *Ih*—*Ij*, the results, given in Table II for chloroalane, do not differ from that obtained with other reagents. In the case of the compound *Ig*, the population of *IIIg*, 3-chlorotetrahydrofuran (*V*), 4-(β-chloroethoxy)-1-butanol (*VI*) and *IIIb* changes from 60 : 6 : : 18 : 16 (ratio 3 : 1) to 34 : 6 : 30 : 30 (ratio 1 : 4).

Determination of Relative Hydrogenolysis Rates of the Acetals *I*

The catharometer response was determined by gas–liquid chromatography of equimolecular mixture of the starting acetal *I* and its hydrogenolysis product *III* or *V* with the acetal *Id* and the

alcohol *IIId*. In order to determine the relative rates, an equimolecular mixture of the acetal *Ia*—*Ic* and *Ie*—*Ij* with 0·001 mol of the acetal *Id* was diluted with ether to the volume 3 ml and introduced into a solution of the reducing agent, prepared from aluminium chloride (0·0005 mol) and lithium aluminium hydride (0·0005 mol) as described above, refluxed 2, 3 and 5 hours and decomposed by a careful addition of 10% aqueous KOH (5 ml). The ethereal layer was separated, the aqueous one was extracted with 5 ml portions of ether till the extract did not contain any starting acetals or their hydrogenolysis products, and the combined ethereal layers were analysed. The results, obtained from the ratio of the reaction products after 2, 3 and 5 hours were practically identical and the given k_{rel} values are the average of these three determinations. In order to determine the relative hydrogenolysis rates of *cis-Ia* and *trans-Ia*, the reaction of the equilibrium mixture of both epimers of *Ia*, together with the acetal *Id*, was followed using the method of internal standard, and the values of k_{rel} were determined from the concentration decrease of the starting compounds.

RESULTS AND DISCUSSION

The acetals *Ia*–*Ij* react with chloroalane in diethyl ether more slowly than the corresponding 2-alkoxytetrahydrofurans[10]: in order to achieve the same conversion in a comparable time, it is necessary to carry out the reaction in boiling ether instead of at room temperature. Table II shows the results obtained by following (VPC) the reduction of the acetals *I* till the complete conversion. The reduction proceeds unequivocally in the case of all the acetals *I*, except 3-chloro-2-(2-chloroethoxy)tetrahydrofuran *Ig*. The reduction of acetals containing alkyl groups and ω-chlorobutyl groups (*Ia*–*If*) follows the pathway *A* to give the corresponding 4-alkoxy-3-chloro-1-butanols *IIIa*–*IIIf*, which do not react further under the reaction conditions; the acetals *Ii* and *Ij* with phenyl and trifluoroethyl group are reduced according to the pathway *B*, giving 3-chlorotetrahydrofuran *V*, which is also stable under the reaction conditions. Reduction of 3-chloro-2(2-ethoxy)tetrahydrofuran (*Ih*) affords 4-(2-ethoxy)-1-butanol (*IV*) as the sole product. We assume that the reaction intermediate is 2-(2-ethoxyethoxy)-tetrahydrofuran (*VII*) (which under the reaction conditions is rapidly hydrogenolysed to the compound *IV*) because we were not able to detect the anticipated reaction product, 3-chloro-4-(2-ethoxyethoxy)-1-butanol (*IIIh*) by gas–liquid chromatographic analysis of the reaction mixture at various reaction stages. Only the compound *Ig* affords a mixture of products which contains, in addition to the expected 3-chloro-4-(2-chloroethoxy)-1-butanol (*IIIg*) and the compound *V*, also 4-(2-chloroethoxy)-1-butanol (*VI*) and 3-chloro-4-ethoxy-1-butanol (*IIIb*). Gas–liquid chromatographic analysis of the reaction mixtures at various reaction stages shows that the compounds *VI* and *IIIb* certainly arise by the subsequent hydrogenolysis of one of the chlorine atoms in the compound *IIIg*, however, their formation *via* 3-chloro-2-ethoxytetrahydrofuran (*Ib*) and 2-(2-chloroethoxy)-tetrahydrofuran (*VIII*) cannot be excluded. The compound *Ib* is really detectable during the reaction, though in very small amount. Although the reactions of compounds *Ig*, *Ii* and *Ij* are preparatively unimportant, they are of interest from the

point of view of the studied reaction. The compounds *Ig* and *Ij* are the first tetrahydrofuran acetals with a group other than aryl or benzyl, which undergo hydrogenolysis, one partially and the other completely, on the exocyclic C—O bond (path *B*). The results of the preparative experiments are given in Table I.

The change in the ratio of lithium aluminium hydride to aluminium chloride from 3 : 1, 1 : 1, 1 : 3 to 1 : 4, (alane, chloroalane, dichloroalane and its mixtures with aluminium chloride) had no effect on the direction of cleavage in acetals *Ia*–*If* and *Ih*–*Ij*. In the case of the acetal *Ig*, the amount of the monochlorinated products *VI* and *IIIb* increases with increasing amount of aluminium chloride.

Since for our considerations about the reaction course it is important to know first of all how the reactivity of the acetals *I* depends on the substituent R, we determined the relative hydrogenolysis rates by means of gas–liquid chromatography. The obtained values, given in Table II, were correlated with σ^* constants of the substituents R (Fig. 1). Since the values of σ^* for R = $(CH_2)_4Cl$ and R = $(CH_2)_2.OC_2H_5$ are not known, we calculated the first value using the relation $\sigma^*(CH_2)_4Cl = \sigma^*(CH_2)_2Cl/2{\cdot}78^2 = 0{\cdot}05$; the second value was estimated from $\sigma^*(CH_2)_2OCH_3$ to be 0·15–0·25. The obtained correlation is satisfactory for all substituents R, which cause the exclusive cleavage of the acetals *I* according to the path *A*. The found reaction constant ϱ^* for the cleavage of the endocyclic bond in the compounds *I* is −1·25. The fact that *cis*-3-chloro-2-methoxytetrahydrofuran (*cis-Ia*) is hydrogenolysed faster than the corresponding *trans-Ia* is analogous to *e g.* hydrogenolysis[14] and acid-catalysed hydrolysis[32] of 2,4-disubstituted 1,3-dioxolanes and reflects obviously the easier approach of the reagent to the *cis*-isomers.

Let us consider first the deviation from the linear dependence in the case of the acetal *Ih*. Since the compound *Ih* reacts by way other than that for which the correlation holds, we cannot expect any fit. The fact that the reaction of *Ih* is signifi-

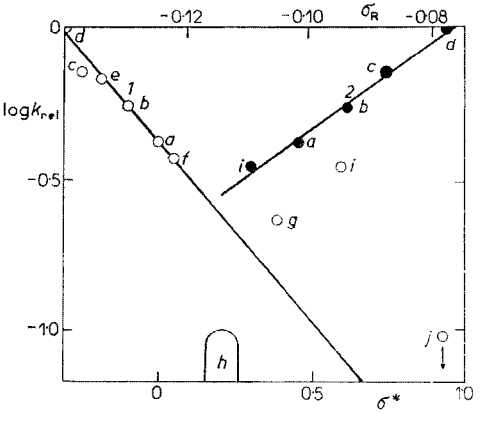


FIG. 1

Plot of log k_{rel} for the Hydrogenolysis of Acetals *I* by Chloroalane against σ^* and σ_R Values

1 σ^* (correlation coefficient for the points *a*—*f* 0·9902); *2* σ_R (correlation coefficient 0·9915).

cantly slower than expected for *IIIh* as intermediate is interpreted as further indication that the acetal *Ih* is not reduced *via* the alcohol *IIIh*. Since the hydrogenolysis of the acetals *Ig*, *Ii* and *Ij* follows partly or completely the pathway *B*, we cannot expect any correlation. The higher reaction rate of the compound *Ig* than that expected for its endocyclic cleavage to *IIIg* can be interpreted by the fact that only 6% of the compound *Ig* react according to the pathway *B*. The cleavage according to the path *B* contributes therefore only negligibly to the rate of consumption of the compound *Ig* and the higher hydrogenolysis rate again shows that the compound *Ig* is consumed also by the formation of compounds *Ib* and *VIII*.

The slope of the correlation straight line corresponds to the assumption that the endocyclic cleavage of the acetals *I* is controlled by the formation of alkoxycarbenium ions A_2 by a process accelerated by electron-donating substituents. The absolute value of the constant ϱ^* shows that the endocyclic cleavage of compounds *I* is relatively little affected by substituents: from this one can judge that the stage of cation A_2 is relatively well developed.

If we plot the relative rates, given in Table II, against σ_R constants of substituents R for which these constants are known (compounds *Ia*–*Id* and *Ii*), we obtain a satisfactory correlation (Fig. 1). In contrast to the correlation using σ^* values, this correlation is valid also for 3-chloro-2-phenoxytetrahydrofuran (*Ii*). This probably indicates that the transition state of the reaction-controlling step has the same character – a developing positive charge at oxygen – in the reaction of the acetals *Ia*–*Id*, which are cleaved at the endocyclic C—O bond, as well as in the reaction of the acetal *Ii*, which reacts at the exocyclic C—O bond. This corresponds to the intermediate A_2 for the compounds *Ia*–*Id* and to the intermediate B_1 for the compound *Ii*. Such an interpretation leads to the conclusion that the reaction of the compound *Ii* is the first case of a reaction with chloroalane in which the rate-controlling step is the formation of a complex between the substrate and reagent. We can assume, as expressed already somewhat differently by Loewen and Brown[11], that this behaviour is caused mainly by the π-electron system of the aromatic nucleus, to which the haloalane is primarily associated so strongly that *1*) the complexation of further haloalane molecule with oxygen atoms of this complex does not take place, and *2*) transformation of this complex into a complex of the type B_1 is very slow.

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REFERENCES

1. Donkas H. M., Fontaine T. P.: J. Amer. Chem. Soc. *73*, 5917 (1951); *75*, 5355 (1953).
2. Eliel E. L.: Record Chem. Progr. *22*, 129 (1961).
3. Ashby E. D., Prather J.: J. Amer. Chem. Soc. *88*, 729 (1966).
4. Eliel E. L., Delmont D. W.: J. Amer. Chem. Soc. *80*, 1744 (1958).

5. Bhattacharjee S. S., Gorin P. A. J.: Can. J. Chem. *47*, 1195 (1969).
6. Diner U. E., Brown R. K.: Can. J. Chem. *45*, 2547 (1967).
7. Zajac W. W., jr, Byrne K. J.: J. Org. Chem. *35*, 3375 (1970).
8. Zajac W. W., jr, Byrne K. J.: J. Org. Chem. *37*, 521 (1972).
9. Eliel E. L., Nowak B. E., Daignault R. A., Badding V. G.: J. Org. Chem. *30*, 2441 (1965).
10. Loewen P. C., Makhubu L. P., Brown R. K.: Can. J. Chem. *50*, 1502 (1972).
11. Loewen P. C., Brown R. K.: Can. J. Chem. *50*, 3639 (1972).
12. Loewen P. C., Zajac W. W., jr, Brown R. K.: Can. J. Chem. *47*, 4059 (1969).
13. Leggetter B. E., Diner U. E., Brown R. K.: Can. J. Chem. *42*, 2113 (1964).
14. Leggetter B. E., Brown R. K.: Can. J. Chem. *43*, 1030 (1965).
15. Leggetter B. E., Brown R. K.: Can J. Chem. *42*, 1005 (1964).
16. Leggetter B. E., Brown R. K., Can. J. Chem. *42*, 990 (1964).
17. Pettit G. R., Bowyer W. J.: J. Org. Chem. *25*, 84 (1960).
18. Eliel E. L., Nowak B. E., Daignault R. A.: J. Org. Chem. *30*, 2448 (1965).
19. Leggetter B. E., Brown R. K.: Can. J. Chem. *41*, 2671 (1963).
20. Frainet E., Calas R., Bazoun A.: Bull. Soc. Chim. Fr. *1960*, 1480.
21. Trofimov B. A., Atavin A. C., Orlova C. E., Kosicina E. I., Kojko V. V.: Izv. Akad. Nauk SSSR, Ser. Khim. *1967*, 2727.
22. Fleming B., Bolker H. I.: Can. J. Chem. *52*, 888 (1974).
23. Cordes E. H., Bull H. G.: Chem. Rev. *74*, 581 (1974).
24. Hammond G. S.: J. Amer. Chem. Soc. *77*, 334 (1955).
25. Felkin H.: Bull. Soc. Chim. Fr. *1951*, 347.
26. Normant H.: C. R. Acad. Sci., *229*, 1848 (1949).
27. Zezula V., Kratochvíl M.: This Journal *35*, 1745 (1970).
28. Lorrette U. B.: J. Org. Chem. *23*, 1950 (1958).
29. Kratochvíl M.: This Journal *25*, 1351 (1960).
30. Kratochvíl M.: This Journal *27*, 742 (1962).
31. Crombie L., Gold J., Harper S. H., Srokes B. J.: J. Chem. Soc. *1956*, 136.
32. Salomaa P.: Ann. Univ. Turku, Ser. A *46*, 15 (1961); Chem. Abstr. *55*, 12387 (1961).

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